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A new thin-film electroluminescent material— $ZnF_2 : Mn^*$

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Both ac and dc orange (580 nm) electroluminescence (EL) are reported for thin films of $ZnF_2 : Mn$ sandwiched between SiO semi-insulating films. All layers are formed by vacuum evaporation and no postdeposition annealing is required. Unique power input and efficiency vs. frequency characteristics are observed, in part due to the 0.1-s lifetime of excited Mn in ZnF_2 ; hysteresis in the brightness-voltage characteristic occurs. The brightness and power efficiency are found to be, respectively, $10 fL$ and 0.5% under suitable operating conditions.

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High-field collision-excitation electroluminescence (EL) has become a current area of active research as a result of the application of thin-film technology to form relatively stable EL devices with power efficiencies approaching 1% and with hysteresis in the brightness-voltage characteristic permitting information storage as well as display.¹ The major research has involved evaporated $ZnS : Mn$ sandwiched between sputtered or electron-beam evaporated Y_2O_3 ¹⁻³; similar devices have been made with $ZnSe : Mn$ ⁴; related work has been reported on crystals of $CdF_2 : Mn$ in MIS structures⁵; EL has been studied with rare earth dopants in place of Mn in these materials⁶—in all the aforementioned, a high temperature postgrowth anneal is required.

$ZnF_2 : Mn$ is unique among luminescent materials in being capable of rather efficient cathodoluminescence in the form of transparent thin films formed by vacuum evaporation.⁷ No postdeposition anneal is needed. Its lower refractive index minimizes the internal trapping of the emission which reduces substantially the efficiency of ZnS thin films. The ZnF_2 and $ZnF_2 : Mn$ have the rutile structure and are weakly *N*-type semiconductors with low electron mobility.⁸

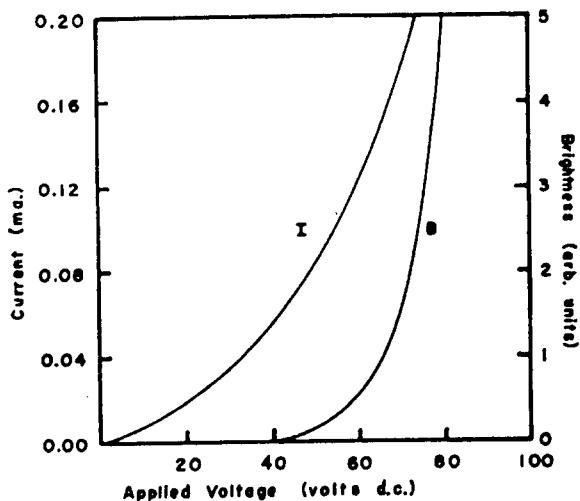


FIG. 1. Current I and brightness B versus applied dc voltage V for $ZnF_2 : 0.011 Mn$ with the typical SiO and fluoride thicknesses.

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thus, these materials differ markedly in structure and electronic properties from CdF_2 and $CdF_2 : Mn$.

The layered thin films were deposited in sequence on conducting Corning glass 7059 (SnO_2 coated to 100Ω /square resistance) maintaining the vacuum at less than 2×10^{-5} Torr. Both the $ZnF_2 : Mn$ and SiO were outgassed before evaporation. The $ZnF_2 : Mn$ used in the evaporation had been mixed by weight from ZnF_2 and MnF_2 , sintered at $800^\circ C$ and ground to a powder. Compositions investigated were 0.5–5-mol% MnF_2 . The substrate was slightly above room temperature. Typical sequential deposits were 5000 \AA of SiO , 2000 \AA of $ZnF_2 : Mn$, and 5000 \AA of SiO . Selected edges were masked in order to make electrical contacts. Finally, the second electrode of aluminum was deposited by evaporation through a mask.

The SiO is only semi-insulating, so that dc EL, as well as ac EL, is observed. The highest efficiencies are measured at low frequencies, e.g., 10 cps. The current I in the external

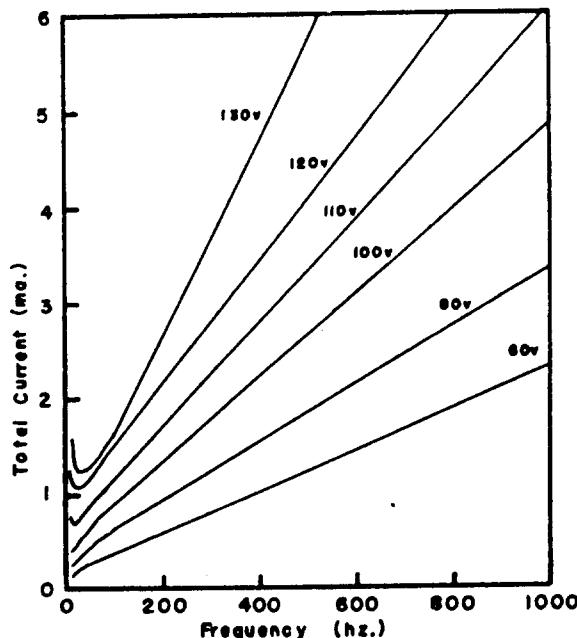


FIG. 2. Total current I versus frequency f for different applied ac voltages V_{ac} . 90% of the data points fall within ± 20 cps and ± 0.1 ma for the curve at highest V and within ± 10 cps and ± 0.02 ma for the curve with lowest V .

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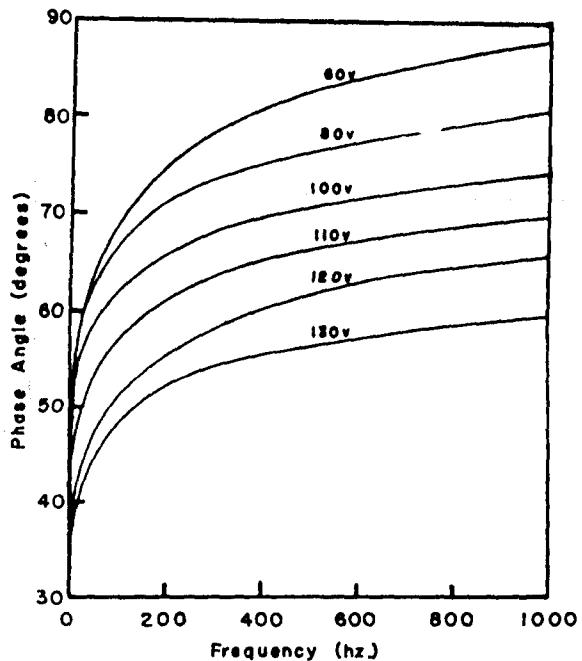


FIG. 3. Phase angle ϕ versus frequency f for different V_{app} . 90% of the data points fall within ± 20 cps and $\pm 3^\circ$ of the fitted curves.

circuit is shown in Fig. 1 for dc, and as a function of frequency for applied ac voltages V in Fig. 2. The brightness, B versus V is also shown on Fig. 1. In order to obtain the input power P for ac the phase difference ϕ between I and V was measured on a dual trace Tektronix 545 scope and is plotted versus f in Fig. 3 for different V . The device responds electrically like a non-Ohmic resistor in parallel with a capacitor so that with increasing f the current generally becomes more capacitive, but at higher V the current remains more resistive to higher f . The non-Ohmic character is evident from the dc measurements. Thus, from the data in Figs. 2 and 3, the P can be obtained: $P = IV \cos\phi$. Except for some structure at low f , P is approximately linear with f , with greater slope at higher V .

The brightness B was measured as a function of V and f . Hysteresis in $B(V)$ was observed and is shown in Fig. 4. This characteristic is similar to those reported for $ZnS : Mn^{1,2}$ and for $ZnSe : Mn^1$. The electrical characteristics described in the preceding paragraph are for the decreasing voltage $B(V)$ curve. The emission spectrum of the $ZnF_2 : Mn$ with EL excitation is the same as previously reported for photo- and cathode-ray excitation, peaking at 580 nm.¹

Absolute brightnesses were measured by two independent methods: comparison with a standard lamp illuminating a diffusing screen, and a calibrated Tektronix J16 digital photometer. Brightnesses of 10 fL were attained with reasonable stability; higher values resulted in deterioration of present devices. Combined with power input data, power efficiencies η of 0.5% were obtained at low frequencies, e.g., 10–30 cps. At higher f , η decreases approximately as $1/f$.

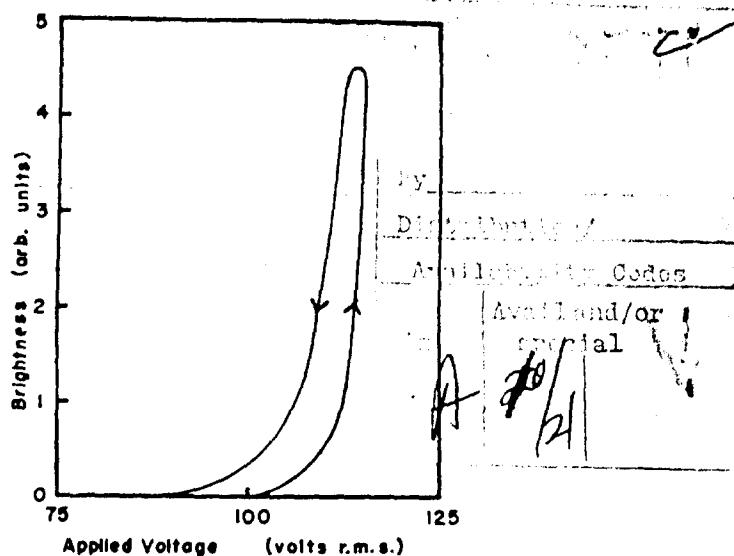


FIG. 4. Brightness-voltage hysteresis curve at 500 cps for $ZnF_2 : 0.016\text{ Mn}$.

The $\eta \propto 1/f$ and $P \propto f$ at the higher f mean, of course, constant B at constant V , independent of f , suggesting saturation. From the radiative lifetime of 0.1 sec for Mn in $ZnF_2 : Mn'$ and for concentrations of 1-mol% Mn, saturation of a 2000-Å-thick layer is predicted at 10 mW of radiation/cm². We observe as much as 0.1 mW/cm² of radiation which means that 1% of the Mn are homogeneously excited simultaneously or that 1% of the volume is excited to saturation. This estimate neglects internal trapping and absorption in the SiO. No inhomogeneities were observed microscopically under normal conditions of excitation.

Summarizing, layered thin-film $ZnF_2 : Mn$ device electroluminescence at low frequencies with efficiencies approximately equal to those of other high field EL devices and with hysteresis in the $B(V)$ characteristic have been observed. We are investigating $ZnF_2 : Mn$ devices with better insulating layers to attain higher efficiency and stability. The absence of a postdeposition anneal allows for the possibility of deposition on low melting substrates such as plastics.

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¹T. Inoguchi and S. Mito, in *Topics in Applied Physics*, edited by J. Pankove (Springer, Heidelberg, 1977), Vol. 17, chap. 6, p. 202.

²V. Marullo, W. Rühle, and A. Onton, *Appl. Phys. Lett.* 31, 452 (1977).

³J.M. Hurd and C.N. King, *J. Electron. Mater.* (to be published).

⁴J. Shah and A.E. DiGiovanni, *Appl. Phys. Lett.* 33, 995 (1978).

⁵T. Langer, B. Krukowska-Fulde, and J.M. Langer, *Appl. Phys. Lett.* 34, 216 (1979).

⁶J. Benoit, P. Benalloul, R. Parrot, and J. Mattler, *J. Lumin.* 18/19, 739 (1979).

⁷F.E. Williams, *J. Opt. Soc. Am.* 37, 302 (1947).

⁸J.H. Crawford and F.E. Williams, *J. Chem. Phys.* 18, 775 (1950).

⁹F.E. Williams and H. Eyring, *J. Chem. Phys.* 15, 289 (1947).